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URANIUM AND THORIUM DECAY SERIES NUCLIDE ABUNDANCES IN MARINE PLANKTON

Karl K. Turekain, et al

Yale University

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URANIUM AND THORIUM DECAY SERIES NUCLIDE ABUNDANCES

IN MARINE PLANKTON

Principal Investigator: Karl K. Turekian

Coinvestigators: D. P. Kharkar

John Thomson

Department of Geology and Geophysics

Yale University

New Haven, Connecticut 06520

Telephone: 203-436-0377



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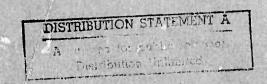
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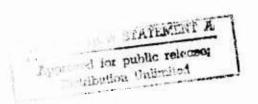
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SUMMARY

A procedure for the analysis of marine plankton for selected members of the uranium and thorium decay series has been developed.

The ${\rm Po}^{210}$ and ${\rm Pb}^{210}$ concentrations of plankton when compared to surface sea water concentrations of these two nuclides can be used to determine the regional aerosol ${\rm Pb}^{210}$ flux to the oceans and the mean residence times of ${\rm Po}^{210}$ and ${\rm Pb}^{210}$ as they are removed by settling planktonic debris in surface waters of various regions of the world oceans.

The ${\rm Po}^{210}/{\rm Pb}^{210}$ activity ratio in plankton reflects the ambient oceanic value which in turn is related to the productivity. The ${\rm Th}^{228}/{\rm Ra}^{228}$ activity ratio of plankton yields similar results. As the ${\rm Ra}^{228}$ comes from shelf sediments free of its daughter, ${\rm Th}^{228}$, the ratio of ${\rm Th}^{228}/{\rm Ra}^{228}$ in the water also reflects distance from source of injection of the ${\rm Ra}^{228}$.

The Ra^{226} concentration of plankton varies widely over the ocean but generally is higher in the phytoplankton-enriched samples. Its concentration can be used to assess the Ra^{228} concentration in plankton once the regional surface sea water ratio of $\mathrm{Ra}^{228}/\mathrm{Ra}^{226}$ is known.

In regions of upwelling the deep water shows a deficiency of Po^{210} (and presumably Pb^{210}) relative to Ra^{226} . This is attributable to the large flux of particulates raining down from above in such highly productive regions.

The ${\rm Th}^{228}$ concentration of plankton permits an estimate of the maximum ${\rm Th}^{234}$ concentration in plankton. Pa 234 , the 1.16 minute half life daughter of ${\rm Th}^{234}$, is the major high energy γ emitter in plankton aside from potassium. A large γ "hot spot" is not expected from this source in plankton particles and is probably not a source of major background for towed scintillation detectors.

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I. AIM OF STUDY

The aim of this study has been to determine the concentrations of members of the uranium and thorium decay series in marine plankton over large areas of the Atlantic Ocean and to use this information in oceanographic problems. These radionuclides are partitioned in different ways between sea water and plankton and particulates in the ocean column, and this fact can be used to assist in the understanding of: (1) surface ocean circulation patterns, and (2) the sources and sinks of the nuclides in the oceans.

The accomplishment of these two goals also provides an opportunity for the assessment of the expected dosages in plankton of the three different types of radiation, α , β , and γ as a function of geography. In principle, although the γ activity in particles can be obtained by direct measurement of plankton, the short half lives of the major γ emitters, Po^{210} and Th^{234} (Pa^{234}), are best estimated from geochemical inferences of the sort derivable from this study.

II. PLAN OF STUDY

The study is divided into three major efforts: (1) the choice of nuclides to be determined and the development of a scheme to analyze marine plankton for these nuclides; (2) the collection of a suite of plankton samples to be analyzed for these nuclides; and (3) the interpretation of the results of these analyses.

The members of the $\rm U^{238}$, $\rm U^{235}$, and $\rm Th^{232}$ decay series are shown in Table 1. The nuclides chosen for study on the basis of geochemical and half-life arguments are the following: for the $\rm Th^{232}$ decay series, $\rm Th^{232}$, $\rm Ra^{228}$, and $\rm Th^{228}$; for the $\rm U^{238}$ decay series, $\rm U^{238}$, $\rm Th^{234}$, $\rm U^{234}$, $\rm Ra^{226}$, $\rm Pb^{210}$, and $\rm Po^{210}$.

We actually were able to measure ${\rm Th}^{234}$ in only one sample because of its short half life (24 days) and the normally long time lapse between sample collection and analysis. We also made only a few measurements of the ${\rm Ra}^{228}$ activity because of its low concentration. We were confident that the measurement of the ${\rm Ra}^{226}$ activity would give us some information on ${\rm Ra}^{228}$, should we need it, based on surface sea water values of the ${\rm Ra}^{228}$ / ${\rm Ra}^{226}$ activity ratios in the Atlantic that were being reported in the literature by others at the time of our work.

The collection of the plankton samples was done primarily by others and either shipped directly back to us or made available to us from collections already made. All the samples we report on are ones that were analyzed sufficiently rapidly after collection to permit the determination of unsupported Po^{210} (138 day half life).

The interpretation of the results is presented as a series of selfcontained reports, some of which have already been submitted for publication.



Table 1: The uranium and thorium decay series.

		U-238	Th-232 SERIES U-235 SERIES											
Np												<u> </u>		
U	U-238	U-234								U-235				
Pa		Po-234									Pa-231		-	
Th	Th-234	Th-230 75 (10 y			Tn·232		Th 228			Th-231		Tr-227		
Ac						Ac:228					Ac-227			
Ra	(3)	Ro-226 1522 ,			Ra 228		Ra 224					Ro 223		
Fr														
Rn	14	An-222					Rn 220				-	Rn-219		
Αt												1		
Ро		Fo18	12:214 16:10	Fa-110			L 		Po-2 2			°o-215		
Bi		įE	1 1 1	1-210		-	1	91-212 60.5 =	1			1	B1-211	
Pb		Pb-214	Pb-2.0	Pb 208			-¥		P5-208			Pb·211	-	Fb-2-37
TI				127				11-208 31m	eli-upa			361m.	Ti-207	

Our analytical scheme for the determination of as many radionuclides of the uranium and thorium decay series of interest as possible was constrained by the fact that normally only about one gram of dry plankton was available for our work from any one location. The problem then was to develop techniques which were mutually compatible and provided the maximum accuracy of measurement for the expected low levels of radioactivity. Three areas of development were required to solve this problem:

- (1) A high yield reliable method of chemical separation for the nuclides of interest had to be developed which could be done on single aliquot of plankton.
- (2) Counting systems with the proper capabilities for low level counting of α and β radiation had to be established.
- (3) Calibration of appropriate standards and spikes had to be effected to assure the accuracy of the measurements.

Although the development of each of these categories occurred simultaneously, they are separated in this report to feature the peculiar problems of each.

The normal "flow sheet" for the analysis of plankton from **th**e moment we receive it in our laboratory to the final result is presented in the last section.

A. The details of the procedures

1. Chemical separation sequence

a. Polonium analysis

From the extensive study of Flynn (1968) it was evident that the polonium analysis should be performed first in the separation sequence because of the element's tendency to absorb on glassware. In addition, the volatility of the element at temperatures as low as 150°C suggested that it would be better to wet ash the plankton samples, and to use an artificial polonium isotope as spike. Po²⁰⁹ would have been preferred because of its halflife and α energy, but Po²⁰⁸ was chosen because it was commercially available.

Preliminary experiments with Po 208 and Po 210 in 1 $\overline{\rm M}$ HCl solutions confirmed that polonium was plated quantitatively on Ag discs after 4 hr. at $\sim 80^{\circ}{\rm C}$ (Flynn, 1968). Analysis of a large plankton sample, half of which had been dry ashed at 600°C then spiked, the other half of which had been

spiked then wet ashed with ${\rm HNO_3-HC10_4}$ mixture, showed that the former aliquot had lost 50% of its ${\rm Po}^{210}$.

A problem with Fe³⁺ in plankton solutions, which caused discoloration of the Ag disc and a consequent loss of polonium α spectra resolution, was eliminated by reducing Fe³⁺ ion with \sim 100 mg ascorbic acid before plating. To prevent polonium plating on both sides of the Ag disc, Teflon tape (initially a Teflon spray coating) was used to mask one side of the disc and the plate recessed (unmasked side up) in a small Teflon holder. Finally, the added ascorbic acid began to show signs of breakdown after 3 hours at 80°C, so this appeared a good compromise period between plating efficiency and good alpha resolution.

The polonium isotopes, Po 208 (α , 5.11 MeV) and Po 210 (α , 5.30 MeV) were readily resolved by α spectrometry.

b. Ra²²⁶ analysis

It was decided to perform two Ra^{226} analyses on each sample, one strictly to determine Ra^{226} after the polonium determination and one to ascertain whether there had been any loss of Ra^{226} (and consequently Ra^{228}) in the subsequent ion exchange procedures (i.e. using Ra^{226} as a tracer for Ra^{228}). The simplest method for Ra^{226} analysis is measurement of the a activity of Rn^{222} after a known storage time, when the fractional radicactive build-in with Ra^{226} can be calculated (Lucas, 1964).

In preliminary experiments using an apparatus similar to that of Bhat (1970), it was found that continuous flow bubbling of helium through standard solutions gave variable yields either because of incomplete removal of Rn^{222} from solution or incomplete trapping of Rn^{222} in the liquid nitrogen trap because of flow rate. This difficulty was overcome by installation of

a peristaltic pump which recirculated the helium repeatedly through the system. The ZnS(Ag) coated cells containing Rn 222 in \sim 38 cm Hg helium were counted at least 4 hr. after filling on a Teledyne-Isotopes Radon Counting System, Type 102, at which time radioactive equilibrium had been achieved by short lived α emitting daughters of Rn 222 .

c. Uranium analysis

The first step in uranium analysis was performed by anion exchange after the Ra 226 analysis at high acid molarity (8 $\overline{\text{N}}$ HCl). The subsequent solvent extraction and plating techniques are essentially those of Ku (1965, 1966). Uranium mounts were analysed by α spectrometry, and the principal α energies (U 238 , 4.19 MeV; U 234 , 4.77 MeV; U 232 , 5.32 MeV) were readily resolved.

One problem which exists in uranium analysis is that the most suitable spike isotope is ${\tt U}^{232}$. Unless freshly purified, this isotope is accompanied by its daughter, ${\tt Th}^{228}$ (t_{1/2} = 1.91 yr), one of the nuclides of interest in this study. Thus if this spike is used, ${\tt Th}^{228}$ values for plankton are unobtainable. If ${\tt Th}^{230}$ spike is used instead ${\tt U}^{232}$ - ${\tt Th}^{228}$, only the ${\tt U}^{234}/{\tt U}^{238}$ activity ratio can be determined in a uranium analysis.

Spiked uranium analyses yielded chemical efficiencies of 50-70%.

d. Lead analysis

Lead was separated after uranium by anion exchange from 1.5 $\overline{\rm M}$ HCl, following the method of Rama et al. (1962). Mounts for β^- counting to follow the radioactive build-in of Bi²¹⁰ were prepared by mounting PbCrO₄. The chemical efficiency of separation was 65-90%.

e. Th analysis

Thorium separations were made by an anion exchange method from 7 $\overline{\text{N}}$ HNO

solution as described by Bhat (1970). The purified thorium was mounted for α spectrometry by the method of Ku (1966), and the principal α energies (Th²³², 4.01 MeV; Th²³⁰, 4.68 MeV; Th²²⁸, 5.42 MeV) were readily resolved. Chemical efficiencies from thorium analyses spiked with Th²³⁰ were 60-80%.

f. Ra²²⁸ analysis

 ${
m Ra}^{228}$ was determined by chemical separation of its daughter ${
m Ac}^{228}$ (${
m S}$, ${
m t}_{1/2}$ = 6.13 hr) and following the decay of ${
m Ac}^{228}$ (S. Krishnaswami, personal communication to D.P.K.) ${
m Ac}^{228}$ was adsorbed on a Fe(OH) $_3$ precipitate, roasted and deposited as a slurry on a 3.3 x 1.1 cm. Lucite planchette. The planchette was then counted for decay of ${
m Ac}^{228}$ on a Lal type flow gas counter. The chemical separation of ${
m Ac}^{228}$ on Fe(OH) $_3$ and the physical transfer of Fe(OH) $_3$ to the planchette were assumed quantitative.

2. Counting systems

a. Alpha spectrometers

Two alpha spectrometers are used in this study, providing three counting channels, all with 450 mm² silicon surface barrier detectors. The dual system comprises two ORTEC 101-201 preamplifier-amplifier combinations fed to the halves of the memory of a TMC 400 channel analyzer. Background levels on the detectors of this system are too high in the ${\rm Th}^{228}$ peak region ($\sim 0.01~{\rm cpm}$) to be used in this study, and this spectrometer is used for polonium and uranium analyses only.

The second spectrometer has a new detector, and is used specifically for thorium analyses. This system consists of a Canberra #808 preamplifier, #816 amplifier, and #1461 biased amplifier, fed to a Nuclear Data 128 channel analyzer. Background in the Th 228 peak region is 0.003 cpm.

The full width half maximum resolution of all three spectrometer

channels is in the range 60-80 keV on normal mounts counted for a few days.

b. Gas flow alpha proportional counter.

This system was used in the calibration of the Po^{208} spike, and routinely to give a quick indication of the level of activity on other alphamounts. It consists of an NMC PCC 10A Proportional Counter Converter (2.25" diameter chamber) coupled to a TMC SG - 2A combined high voltage supply and scaler.

P-10 (10% CH₄ in Ar) is used as flow gas, and gives a background of ~ 0.09 cpm on the alpha plateau at 1150 volts. This counter's α efficiency is 51% as determined by an Am²⁴¹ source on stainless steel.

c. Gas flow beta proportional counter.

This counter is a Sharp LB-100 low level anticoincidence counting system, with a 1.25" diameter 80 $\mu g/cm^2$ Mylar window. It is used exclusively to monitor the growth of Bi 210 (β^- , 1.16 MeV, 5.01 dy.) towards radioactive equilibrium with Pb 210 (β^- , 0.015 MeV, 22 yr.) in lead mounts. Two counting windows are used, with a total background of 0.50 \pm 0.01 cpm using P-10 as flow gas. Counting efficiency for Bi 210 (\sim 30 mg PbCrO $_4$, 5.2 mg/cm 2 Mylar filter for Po 210 α s) is 28%.

d. Gas flow beta geiger counter.

This counter consists of a Lal-type detector and guard detector, with Sharp "Low beta" anticoincidence electronics. It is used exclusively to measure the decay of ${\rm Ac}^{228}$ (${\rm \beta}^-$, 1.11, 6.13 hrs.) in ${\rm Ra}^{228}$ analyses. The inherent counter background is 0.13 \pm 0.01 cpm, operated in the geiger region and flowing Q gas (0.95% isobutane in He). Efficiency for ${\rm Ac}^{228}$ (20 mg. (Fe(OH) $_3$, 80 µg/cm 2 Mylar cover) is 32%.

e. Radon counting system.

This is a commercial system, a Teledyne Isotopes Model 102. The system has two independent counting channels for 125 ml. ZnS (Ag) detector cells. Typical detector backgrounds, rising slightly over a period of two years, are in the range 0.15-0.30 cpm.

3. Laboratory calibrations.

A ${
m Th}^{230}$ spike solution, calibrated at 3.7 dpm/ml, was obtained from Lamont Doherty Geological Observatory. This spike was chosen as our primary reference, and the specific activity was assumed error free. Alpha spectrometry confirmed the solution free from ${
m Th}^{232}$ and ${
m Th}^{228}$; therefore the spike was suitable for these isotopes in plankton analyses.

a. Aged Th^{232} - Th^{228} solution.

To calibrate the ${\rm Ac}^{228}$ chemical separation efficiency and the Laltype counter efficiency for ${\rm Ac}^{228}$, a ${\rm Ra}^{228}$ standard was required. Since none was commercially available, an aged ${\rm Th}({\rm NO}_3)_4$ salt was dissolved in 8 $\overline{\rm N}$ HNO $_3$ and standardized against the ${\rm Th}^{230}$ spike.

Runs with ${\rm Th}^{232}{\rm -Th}^{228}$ solution alone. (Thorium isotopes separated by ion exchange, activity ratios determined by alpha spectrometry.)

	$\mathrm{Th}^{232}/\mathrm{Th}^{228}$	$_{\mathrm{Th}}^{230}/_{\mathrm{Th}}^{232}$	$\mathrm{Th}^{230}/\mathrm{Th}^{228}$
Run 1	0.975 <u>+</u> 0.014	0.120 + 0.004	0.123 + 0.004
Run 2	0.972 <u>+</u> 0.020	- 0.129 <u>+</u> 0.006	0.132 ± 0.006
Run 3	0.995 <u>+</u> 0.020	0.102 <u>+</u> 0.005	0.102 <u>+</u> 0.005
Mean	0.981 <u>+</u> 0.011	0.117 + 0.003	0.119 <u>+</u> 0.003

Runs with 1 ml Th 230 reference solution added to 2 ml Th 232 -Th 228 solution Y.

	$\mathrm{Th}^{232}/\mathrm{Th}^{228}$	$_{\mathrm{Th}}^{230}/_{\mathrm{Th}}^{232}$	$\mathrm{Th}^{230}/\mathrm{Th}^{228}$
Run 1	0.992 <u>+</u> 0.017	0.324 <u>+</u> 0.008	0.327 <u>+</u> 0.008
Run 2	0.984 <u>+</u> 0.023	0.325 <u>+</u> 0.011	0.330 ± 0.011
Run 3	1.016 ± 0.024	0.327 ± 0.011	0.332 <u>+</u> 0.011
Mean	0.997 <u>+</u> 0.012	0.325 <u>+</u> 0.006	0.326 <u>+</u> 0.006

From the mean $(\text{Th}^{228}/\text{Th}^{232})$ activity ratios above, it is evident that the 4n radioactive series is close to secular equilibrium in the solution. The Th^{230} contaminant has a mean activity ratio of 0.118 ± 0.002 relative to Th^{232} and Th^{228} . Addition of 3.7 dpm Th^{230} spike to 2 ml of the solution causes this ratio to increase to 0.326 ± 0.004 .

Then
$$(Th_{contaminant}^{230})/Th^{232} = 0.118 \pm 0.002$$

and, in 2 ml solution Y,

$$(Th_{contaminant}^{230} + Th_{spike}^{230})/Th^{232} = 0.326 \pm 0.004$$

so specific activity of Th^{232} in solution = 3.7/2 (0.208 \pm 0.004)

=
$$8.9 \pm 0.2 \, dpm/ml$$
.

Two aliquots of the ${\rm Th}^{232}{\rm -Th}^{228}$ solution were taken, the thorium isotopes separated by ion exchange, and ${\rm Ac}^{228}$ separated from the resultant solution containing ${\rm Ra}^{228}$. The combined separation and counting efficiency for ${\rm Ac}^{228}$ was determined to be 31.4 \pm 1.8% and 33.16 \pm 1.8% (mean 32.3 \pm 1.3%), based on ${\rm Ra}^{228}$ specific activity of 8.9 \pm 0.2 dpm/ml.

The history of this spike, also obtained from Lamont Doherty Geological Observatory, is well known (Kaufman, 1964; Ku, 1966). Extraction of uranium and thorium by ion exchange from the spike, followed by alpha spectrometric analysis, showed no thorium isotopes other than Th²²⁸ present, and only

 ${\rm U}^{233}$ activity (= 0.024 ${\rm U}^{232}$ specific activity) besides ${\rm U}^{232}$. This spike was used in uranium analyses of plankton samples, and was calibrated against the ${\rm Th}^{230}$ reference solution.

Runs with 1 ml Th 230 reference solution added to 1 ml $\rm U^{232}{\rm -Th}^{228}$ solution:

$$Th^{228}/Th^{230}$$

1.460 + 0.044

1.509 + 0.056

Mean

 1.485 ± 0.036

The mean value of the Th $^{228}/\text{Th}^{230}$ activity ratio corresponds to a Th 228 specific activity of 5.49 \pm 0.13 dpm/ml. Since the purification of U 232 in the spike was performed in 1950, transient equilibrium in the solution has been attained, corresponding to a Th $^{228}/\text{U}^{232}$ activity ratio of 1.03. This yields a value of 5.33 \pm 0.13 dpm/ml U 232 , as of January, 1972.

c. K120a uraninite solution.

This solution was obtained from R. Ku (University of Southern California) who had prepared it from a concordant uraninite in February, 1971. All the 4n+2 series nuclides should be in secular equilibrium with the possible exception of Po^{210} , which could have volatilized during dissolution (Flynn, 1968). The solution was used to calibrate the Sharp proportional counter for Pb^{210} analyses. It itself was calibrated via the U^{232} -Th U^{228} spike.

Runs with 1 ml $\mathrm{U}^{232}\mathrm{-Th}^{228}$ spike added to 1 ml Kl20a.

	$\mathrm{u}^{234}/\mathrm{u}^{238}$	Mean v^{238} , v^{234}/v^{232}	$\mathrm{Th}^{230}/\mathrm{Th}^{228}$
Run 1	1.023 <u>+</u> 0.028	0.974 <u>+</u> 0.026	0.977 <u>+</u> 0.031
Run 2	0.977 <u>+</u> 0.024	0.920 ± 0.022	0.941 ± 0.026
Run 3	0.985 <u>+</u> 0.032	0.941 <u>+</u> 0.030	0.956 ± 0.023
Mean	0.995 <u>+</u> 0.016	0.945 <u>+</u> 0.015	0.958 ± 0.015

From the mean U^{234}/U^{238} activity ratio it is evident the 4n+2 radioactive series is in secular equilibrium in the Kl20a solution. The mean U^{238} , U^{234}/U^{232}) and Th^{230}/Th^{228} activity ratios correspond to specific activities of 5.04 ± 0.15 and 5.26 ± 0.15 dpm/ml (mean 5.15 ± 0.11 dpm/ml) for the 4n+2 series nuclides in the solution.

Aliquots of the K120a solution (1 ml, 2 ml and 5 ml) were used to calibrate the Sharp counter efficiency for Bi 210 . The efficiency found was 28.3 \pm 0.9% based on a Pb 210 specific activity of 5.15 dpm/ml.

d. Rn^{222} extraction and counting efficiency.

The radon extract system used is described above. The combined physical extraction and counting efficiencies for $\rm Rn^{222}$ were determined by standards prepared from an Amersham Searle $\rm Ra^{226}$ solution, a Lamont Doherty Geological Observatory $\rm Ra^{226}$ standard and the Kl20a solution. The results for these standards in various counting vessels on both counting channels are shown below. Corrections are made to the raw data for detector background, $\rm Rn^{222}$ ingrowth from $\rm Ra^{226}$ during storage, and $\rm Rn^{222}$ decay from separation to the midpoint of counting.

Extraction and counting efficiencies of radon in the extraction system and the detectors used.

Vessel	Standard	Efficiency	
		Channel A	Channel B
9	AS 2	93.5 <u>+</u> 0.6	
9	LDGO	91.7 <u>+</u> 0.5	92.5 \pm 0.5
5	AS 2	89.6 <u>+</u> 0.6	92.0 <u>+</u> 0.6
6	AS 3	90.2 <u>+</u> 0.7	90.4 <u>+</u> 0.7
4	LDGO	96.4 <u>+</u> 0.6	93.0 ± 0.9
3	AS 3	94.2 <u>+</u> 0.9	93.5 <u>+</u> 1.1
3	LDGO	91.2 <u>+</u> 0.3	91.1 <u>+</u> 0.5
7	K120a	91.9 <u>+</u> 0.7	89.4 <u>+</u> 0.7
6	AS 2	89.0 <u>+</u> 0.8	91.9 <u>+</u> 0.6
6	AS 3	94.6 <u>+</u> 0.7	93.5 <u>+</u> 0.5
3	LDGO	93.5 <u>+</u> 0.3	
7	AS 2	93.8 <u>+</u> 0.5	92.5 \pm 0.5
5	LDGO	94.9 <u>+</u> 0.5	96.0 <u>+</u> 0.5
14	AS 2	89.0 <u>+</u> 0.5	90.8 <u>+</u> 0.4
9	AS 3	94.1 <u>+</u> 0.5	91.2 <u>+</u> 0.3
8	LDGO	94.3 <u>+</u> 0.3	94.0 <u>+</u> 0.4
6	K120a	91.5 <u>+</u> 0.7	90.6 <u>+</u> 0.6

The efficiency used in calculations from either channel was $92\pm2\%$.

The ${\rm Po}^{208}$ spike obtained from Amersham-Searle was calibrated after plating on Ag discs on the PCC 10 A counter. The count rates of sources

e. Po²⁰⁸ spike calibration.

plated for different times are given below.

Sample (1 ml Po ²⁰⁸)	Plating Time (hours)	Count Rate (inc. background)
Р3	3	1.57 ± 0.04
P24	3	1.59 ± 0.04
P21	16	1.61 <u>+</u> 0.04
P20	4	1.69 <u>+</u> 0.04
P22	4	1.64 + 0.06
P24	4	1.67 ± 0.07
Mean of 4 hr. s	samples	1.67 <u>+</u> 0.03
Counter Backgro	ound	0.09 ± 0.01

The mean 4 hr. sample count rate less background (1.58 \pm 0.03) corresponds to a specific activity of 3.1 \pm 0.1 dpm/m1 Po²⁰⁸ on 3/22/72. Three samples containing 1 ml K120a solution plus 1 ml Po²⁰⁸ spike yielded Po²¹⁰/Po²⁰⁸ ratios of 1.40 \pm 0.05. 1.53 \pm 0.05 and 1.48 \pm 0.04 (mean 1.47 \pm 0.03). With allowance for build-in in the time since preparation of the uraninite solution, this ratio should be 1.7 if no Po²¹⁰ loss occurred in preparation or 1.4 if all Po²¹⁰ was volatilized in preparation. Thus the value determined for the Po²⁰⁸ specific activity appears reasonable.

B. Flow sheet for the analysis of plankton

The plankton samples, usually frozen in seawater, are thaved, filtered on a Büchner funnel, washed with distilled water, and dried at 105°C. Some samples were obtained freeze dried: these were dried at 105°C. After homo-

genization in an agate mortar, a 200-400 mg aliquot of dried plankton was ashed at 600-700°C for 2 hr. and reweighed to give the fraction of inorganic material in the sample. (These ashed aliquots are reserved for neutron activation analysis at a future date.) The remainder of the plankton sample, usually 0.5-2 g, is taken for radiochemical analysis.

The sample is weighed and transferred to a Teflon dish, moistened with distilled water, and concentrated HNO $_3$ added slowly until effervescence ceases. Po 208 and Th 230 or U 232 -Th 228 spikes and Pb carrier are added, and the sample is treated with 25 ml HNO $_3$ and 5 ml. HClO $_4$ concentrated acids to destroy organic matter. The dry residue is again heated to dryness with 10 ml. concentrated HCl, and then leached with 2 x 12 ml. portions of 1 $\overline{\rm M}$ HCl. The solid residue at this stage (usually only present if the sample is siliceous) is treated with 10 ml. 48% HF and a few drops of concentrated HClO $_4$ and heated to dryness. This second dry residue is converted to the chloride form by concentrated HCl, dissolved in a further 2 x 12 ml. 1 $\overline{\rm M}$ HCl, and combined with the first leachates. All apparatus used to this stage is Teflon or polypropylene to avoid polonium absorption on the walls.

To the clear plankton solution in a 100 ml. Teflon beaker (50 ml., $1\ \overline{\text{M}}\ \text{HCl}$), 100 mg. ascorbic acid is added to reduce any Fe $^{3+}$ ion present. A 0.5" diameter Ag disc (0.005"thick), masked on one side with Teflon and recessed in a Teflon plug, is then immersed in the solution, and the solution heated at \sim 80°C for 3 hr., constantly stirred by a Teflon paddle. This stirrer paddle goes through a heavy Teflon lid which reduces evaporation loss from the solution. Polonium plates spontaneously on the disc, which after washing with distilled water and acetone is ready for α spectrometric analysis.

After the polonium separation, the solution is heated with 1 ml. each HNO_3 and HClO_4 added to destroy the ascorbic acid. The residue is dissolved in 50 ml. 8 M HCl and transferred to a radon bubbler vessel. Helium is passed through the solution to purge any radon initially present, and the vessel is then sealed and stored for at least 10 days before Ra^{226} analysis. At the end of this time, helium is passed through the solution in a closed pumping loop, and radon is condensed in a liquid nitrogen trap. At the end of circulation (20 min.), the excess helium is pumped off, the trapped radon is warmed up $\underline{\mathrm{in}}$ vacuo and transferred to a pre-evacuated detector vessel with a slug of helium.

After Rn 222 extraction, the solution is passed through a Dowex AG 1 x 8 anion exchange column (12 cm. x 1 cm., 100-200 mesh) preconditioned with 8 $\overline{\rm M}$ HCl. Uranium isotopes are adsorbed by the resin, and after washing with 2 x 40 ml. 8 $\overline{\rm M}$ HCl are eluted with distilled water. Any Fe $^{3+}$ present is extracted from the uranium fraction in 8 $\overline{\rm M}$ HCl by diisopropyl ether, the uranium is further purified by extraction to ethyl acetate from 4 $\overline{\rm M}$ HNO $_3$ / saturated Al(NO $_3$) $_3$ solution, back extracted into distilled water and finally extracted as a TTA complex in benzene from a HNO $_3$ solution at pH 3. This complex is deposited and flamed on a 1" stainless steel disc for α spectrometric analysis.

The effluent from the uranium column is evaporated to dryness, dissolved in a minimum quantity of 6 $\overline{\rm M}$ HCl, and diluted with distilled water to a 1.5 $\overline{\rm M}$ HCl solution. This solution is passed through a Dowex AG 1 x 8 anion exchange column (12 cm. x 1 cm., 100-200 mesh) preconditioned with 1.5 $\overline{\rm M}$ HCl. Lead isotopes are adsorbed on the column, and after washing with 2 x 30 ml. 1.5 $\overline{\rm M}$ HCl are eluted with distilled water. The pH of the eluate

is adjusted to around 5, PbCrO $_4$ is precipitated by addition of excess ${
m Na}_2{
m CrO}_4$, and the pH readjusted to 5. The precipitate is filtered off, washed with distilled water, and dried at $110^{\circ}{\rm C}$. The PbCrO $_4$ is mounted for ${
m \beta}^-$ counting by deposition as an H $_2$ O slurry on a tared 1" diameter Lucite planchette, dried and reweighed. A 5.2 mg./cm 2 Mylar film is gaued over the planchette to filter Po 210 ${\rm \alpha}$ particles.

The effluent from the lead column is evaporated to dryness, the residue dissolved in 7 $\overline{\rm M}$ HNO $_3$, and the solution passed through a Dowex AG 1 x 8 anion exchange column (12 cm. x 1 cm., 100-200 mesh) preconditioned with 7 $\overline{\rm M}$ HNO $_3$. Thorium isotopes are adsorbed by the column, and after washing with 2 x 40 ml. 7 $\overline{\rm N}$ HNO $_3$ are eluted with 6 $\overline{\rm N}$ HCl. The eluate is taken to dryness, and the thorium isotopes extracted from 0.1 $\overline{\rm N}$ HNO $_3$ solution as a TTA - benzene complex. This complex is mounted for α spectrometric analysis similarly to uranium.

The effluent from the thorium column is evaporated to dryness, dissolved in 250 ml. 1 $\overline{\text{M}}$ HCl, Fe³⁺ calrier added, and Fe(OH)₃ precipitated by ammonia in the presence of 10 mg. Ba²⁺ holdback carrier. The precipitate is discarded and the scavenged solution stored hot for \sim 40 hours to remove Rn²²² and its decay products from the solution and to allow Ra²²⁸ to develop a radioactive equilibrium activity of Ac²²⁸. At the end of this period, Fe³⁺ carrier is again added and Ac²²⁸ adsorbed on the Fe(OH)₃ (20 mg.) precipitated from the solution. The precipitate is filtered, roasted and deposited as a slurry on a tared Lucite planchette for β counting. An 80 µg/cm² Mylar film is glued over the planchette when the precipitate is dry to prevent loss of material.

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IV RESULTS

- A. Uranium and thorium decay series nuclides in plankton from the Caribbean.
- B. The fates of Pb^{210} and Po^{210} in the ocean surface.
- C. ${
 m Pb}^{\,210}$ in coastal waters of the eastern United States.
- D. Ra^{226} in plankton from the Atlantic Ocean.
- E. Po^{210} and Pb^{210} distribution in ocean water profiles from the eastern South Pacific.

A. Uranium and thorium $\operatorname{dec}_{\mathcal{I}_{\mathcal{I}}}$ series nuclides in plankton from the Caribbean.

(Preliminary report)

URANIUM AND THORIUM DECAY SERIES NUCLIDES IN PLANKTON FROM THE CARIBBEAN

D. P. Kharkar, J. Thomson, K.K. Turekian, W.O. Forster

Introduction

The abundances of the members of the uranium and thorium decay series in the oceans can be used to understand both the dynamics of ocean circulation and the influence of particles in the water column on the distribution of elements in ocean water profiles and marine sediments. A major role is played by plankton in these studies both as indicators of surface water radionuclide abundances and as active agents modifying these abundances. We report in this paper a method of determining the abundance of several natural radionuclides in the same small plankton sample, together with data gathered over much of the Caribbean and the inferences drawn concerning the processes responsible for the observed distributions.

The samples were collected on two cruises during the Fall and Winter of 1971-1972 as previously reported by one of us (Forster et al., 1972). All the samples consist predominantly of calanoids and cyclopoids. This relative homogeneity may be expected to minimize effects of differential species uptake of the radionuclides. Figure 1 is an index map of the stations at which samples were obtained for this study.

Analytical Methods

The plankton samples were freeze dried on ship and stored in plastic vials. On arrival at Yale they were dried overnight at 105° C, and homogenized in an agate mortar. The available sample for radiochemical analyses was generally around 1 g, and was used in the following radiochemical procedure for the determination of U^{238} , U^{234} , U^{234} , U^{238} , $U^{$

Sample dissolution

The samples were weighed and transferred to a Teflon dish, moistened with distilled water, and concentrated HNO $_3$ added until effervescence ceased. Po 208 and Th 230 or U 232 -Th 228 spikes and Pb carrier (\sim 40 mg as PbCrO $_4$) were added, and the sample heated to dryness with 25 ml HNO $_3$ - 5 ml HClO $_4$. This residue was taken to dryness with 10 ml HCl, and then leached with 2 x 12 ml 1 $\overline{\rm M}$ HCl. The remaining solid (generally siliceous) was treated with 10 ml HF and a few drops of HClO $_4$ and taken to dryness. This residue was again heated to dryness with HCl, and leached with 2 x 12 ml 1 $\overline{\rm M}$ HCl. This procedure yielded a clear solution in 1 $\overline{\rm M}$ HCl. All apparatus used to this stage was Teflon or polypropylene to prevent absorption of polonium.

Chemical separations

Fe $^{3+}$ in the 1 $\overline{\text{M}}$ HCl plankton solution was reduced with \sim 100 mg ascorbic acid (Francis et al., 1968), and polonium isotopes plated on to a 0.5" diameter Ag disc at 85°C for 3 hours (Flynn, 1968). Next the plankton solution was transferred to a bubbler vessel and purged of Rn 222 with helium. The vessel was then sealed and stored for at least 10 days to develop Rn 222 (Lucas, 1964). The Rn 222 was transferred to a counting cell on an apparatas similar to that of Bhat (1970), with a peristaltic pump to recycle the helium carrier gas. Uranium, lead and thorium were then separated in that

sequence by anion exchange on Dowex Ag 1 x 8. U was separated from 8 $\overline{\rm M}$ HCl solution, and further purified by solvent extraction as described by Ku (1965), (1966). Pb was separated from 1.5 $\overline{\rm M}$ HCl solution, and precipitated as PbCrO₄ at pH 5 [Rama et al., 1961]. Th was separated from 7 $\overline{\rm M}$ HNO₃ solution [Bhat, (1970)]. The solution remaining after the ion exchange steps contained only Ra²²⁸ of the isotopes of interest. Fe³⁺ carrier was added twice and precipitated as Fe(OH)₃ (20 mg). These precipitates were rejected and the solution stored warm at pH 1 in HCl for \sim 40 hours to allow Ac²²⁸ to develop from Ra²²⁸. Ac²²⁸ was then scavenged on Fe(OH)₃, and the precipitate filtered off and roasted.

The purified U and Th fractions were mounted for α spectrometry by extraction of their thermoyltrifluoroacetone complexes in benzene from HNO $_3$ solutions at pH 3 and pH 1.5 respectively [Ku, (1966)]. Chemical yields for U and Th ranged from 50-70% and 60-80% respectively. PbCrO $_4$ was prepared for estimation of Pb chemical yield and β counting by mounting as a slurry on a 1" diameter tared Lucite planchette and was then dried and weighed. Pb yields ranged from 65-90%. The Fe(OH) $_3$ carrier for Ac 228 was also mounted as a slurry on a 3.3 cm x 1.1 cm area on a rectangular Lucite planchette, the chemical separation being considered quantitative.

Counting prodedures

Po, U and Th mounts were counted by α spectrometry, using 450 mm² silicon surface barrier detectors with α resolutions around 75 KeV (f.w.h.m.) over count periods of days. The Ra²²⁶ daughter Rn²²² (α , 3.823 dy) was counted in 125 ml ZnS(Ag) coated cells on a Teledyne Isotopes Type 102 radon counting system. The combined separation efficiency for Rn²²² and counting efficiency for Rn²²² and its daughter α s was 92%. Vessel back-

grounds ranged from 0.15 - 0.30 cpm. Pb 210 was measured via the developed Bi 210 activity (β^- , 5.01 dy.) on a Sharp LB-100 Lowbeta proportional system with a 1.25" diameter detector and 80 $\mu g/cm^2$ Au-Mylar window. The detection efficiency for Bi 210 , with a 5.2 mg/cm Mylar filter for Po 210 αs , was 28% with a background of 0.5 cmp. Ra 228 was determined via Ac 228 (β^- , 6.13 hr.) decay (Moore, 1969) on a rectangular gas-flow Geiger counter (4.2 cm x 1.7 cm; Lal and Schink, 1960), with an anticoincidence guard and Sharp Lowbeta electronics. The combined chemical separation and counting efficiency for Ac 228 was 32% with a background of 0.13 cpm.

Results

Table 1 lists the results obtained on the plankton samples. The errors listed are 1 σ counting errors. Only one sample yielded a measurable Ra 228 value but with a large error. No further attempt at obtaining Ra 228 values was made because of the low activity due to the small size of the samples. As we shall see this is not a great loss since a reasonable estimate of the Ra 228 concentration can be made from the Ra 226 which is compatible with the few numbers obtained here and in other studies. Where U 238 and U 234 activities were determined a U 232 -Th 228 spike was used thus eliminating the possibility of obtaining a value for Th 230 , and similarly when the Th 230 spike was used only the U 234 /U 238 activity ratio could be obtained.

Discussion

The concentration efficiency of plankton in extracting the radio-nuclides from sea water is highest for thorium and lowest for uranium (Table 2). Since the Th²³² content of surface ocean water is so low (Kaufman, 1969) the Th²³² concentration factor may be as much due to the trapping of thorium-rich particulates, as has been suggested for other plankton (Turekian, Katz and Chan, 1973), as adsorption or trapping of an ionic species. The other nuclides are undoubtedly present, at least initially, as ionic species and their relative concentration factors may be more realistic. Of these Pc²¹⁰ is most efficiently concentrated and uranium the least. The sequence is compatible with what is known about the chemical behavior of these nuclides, as expressed for example in the separation scheme described above.

In spite of the homogenous nature of the samples, the specific activities in Table 1 are variable, but patterns emerge when activity ratios of genetically coupled nuclides such as U^{234}/U^{238} , Po^{210}/Pb^{210} or Th^{228}/Ra^{228} are considered. It is these ratios which we use in an attempt to trace the Caribbean surface waters.

 $\underline{\mathrm{U}^{234}/\mathrm{U}^{238}}$: The scatter of $\mathrm{U}^{234}/\mathrm{U}^{238}$ activity ratios is large because of the poor counting statistics derived from the small quantities of uranium. The average of all $\mathrm{U}^{234}/\mathrm{U}^{238}$ activity ratio values, however, is 1.15, the value typical of sea water.

 ${\rm Po}^{210}/{\rm Pb}^{210}$: The distribution of the ${\rm Po}^{210}/{\rm Pb}^{210}$ activity ratio in the Caribbean plankton is shown in Figure 2. Lowest values occur in the southeast, the source of surface waters in the Caribbean. Indeed the ${\rm Po}^{210}/{\rm Pb}^{210}$ map closely resembles Wüst's (1964) surface salinity map for the same region.

This source water at the southeast is the low salinity Guiana Current, coming along the Brazilian coast north of the Amazon. Its track is along a coastal area which may be presumed to be of relatively high productivity.

As shown by the pattern of the ${\rm Po}^{210}/{\rm Pb}^{210}$ activity ratio (Figure 2) the relatively greater extraction of Po relative to Pb by plankton indicates that the source water to the Caribbean is from an area in which biological activity has stripped Po from the water. The gradual increase in the ${\rm Po}^{210}/{\rm Pb}^{210}$ activity ratio away from the plume in the southeast implies a less efficient scavenging flux of ${\rm Po}^{210}$ by plankton throughout the Caribbean or a mixing with North Atlantic water with a low productivity history.

 $\frac{\text{Th}^{228}/\text{Ra}^{228}}{\text{Ra}^{228}}$: Although only one Ra 228 value is listed in Table 1, and that with a large error, it is possible to use the Ra 226 data to obtain a fairly accurate estimate of the expected Ra 228 concentration in the plankton if no fractionation from sea water occurs. The possibility of fractionation is fairly remote in that they are isotopes of an element that is readily soluble at the concentrations found in sea water. We can use the study of Ra 228 abundances in surface waters of the Caribbean made by Kaufman et al. (1973) to obtain an activity ratio of Ra $^{228}/\text{Ra}^{226}$ of 0.47 for Caribbean surface waters. Using this ratio we can obtain the Ra 228 activities of the plankton samples by multiplying the Ra 226 activities by this factor. Szabo (1966) obtained Ra 226 values very similar to these reported here. This has been done in Table 3 where the measured Th $^{228}/\text{Ra}^{228}$ activities are also given together with the attendant Th $^{228}/\text{Ra}^{228}$ activity ratios.

Two features are evident in comparing Table 3 and the index map (Figure 1) showing the locations of the samples. First, the activity ratio of the four samples is unity or less whereas from the concentration factor in Table 2 we would expect a heavy bias towards ${\rm Th}^{228}$, if the ${\rm Th}^{228}/{\rm Ra}^{228}$ activ-

ity ratio were at equilibrium in the water column. This indicates that the source of the Ra^{228} , probably supplied to the Guiana Current by release from sediments on the Brazilian shelf from the mouth of the Amazon northward, is intense (as indicated by the high values of Kaufman et al., 1973) and that very little Th^{228} has had a chance to grow in or survive by the time this water reaches the Caribbean.

Second, there is a trend in the $\mathrm{Th}^{228}/\mathrm{Ra}^{228}$ activity ratio pattern in the Caribbean plankton, supported by the $\mathrm{Th}^{228}/\mathrm{Ra}^{228}$ activity ratio in surface sea water (Broecker et al., 1973). Although many more data are required the samples closest to the presumed site of the Ra 228 migration into the surface water from shelf sediments along the north Brazilian coast have lower ratios than the most remote (northwestward) samples. We believe that this is consistent with the first feature mentioned as well as with the $\mathrm{Po}^{210}/\mathrm{Pb}^{210}$ data discussed earlier. As the water penetrates into the Caribbean from the southeast, Th^{228} grows towards equilibrium with Ra^{228} . The data of Broecker et al. (1973) show the Guiana Current entering the Caribbean with a Th 228/Ra 228 activity ratio around 0.05, which increases to 0.11 at the Yucatan Strait. If biological productivity in the Caribbean were high the efficient extraction of Th^{228} debris settling from the surface would frustrate this trend towards equilibrium. The fact that the Po^{210} ${
m Pb}^{210}$ and ${
m Th}^{228}/{
m Ra}^{228}$ activity ratios show an increasing trend to the northwest indicates that the Caribbean water is less efficient at producing adsorption sites through biological productivity than the water just entering the Caribbean.

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Table 1: Concentration of radioactive nuclides in Caribbean plankton samples

$^{210}_{Po}^{210}_{/Pb}^{210}$	20+2	10+1	15+2	15+2		26+2	21+2	26+2		26+3	16+2		17+2	21+2	9+1	26+4	32+4	24+3	11+1	
$_{ m Po}^{210}$	90+4	61+2	68+3	52+2		64+2	54+2	73+2		81+3	101+4		73+3	71+3	72+3	31+1	74+1	33+1	114+5	
${ m Pb}^{210}$ dpm/g	4.6+0.3	6.4+0.5	4.4+0.4	3.4+0.4	3.1+0.3	2.5+0.2	2.6+0.2	2.8+0.3	3.7+0.3	3.1+0.3	6.2+0.5	7.4+0.5	4.2+0.4	3.4+0.4	8.2+0.5	1.2 ± 0.2	2.3+0.3	1.4+0.2	10.2+0.6	
$_{ m Ra}^{ m 228}$ dpm/g					0.17 ± 0.12															
Ra 226 dpm/g	0.29+0.02	0.14+0.01	0.28+0.02	0.27+0.02	0.15 ± 0.01	0.13+0.01	0.14+0.01	0.16+0.01	0.14+0.01	0.13 ± 0.01	0.15+0.02	0.20+0.02	0.20+0.03	0.63+0.04	0.16 ± 0.02	0.33+0.02	0.84+0.04	0.15+0.01	1.10+0.04	
(Th ²²⁸) dpm/g ex	0.07+0.02			0.10 ± 0.02			0.09+0.08			0.07+0.02										
$_{ m Th}^{232}_{ m dpm/g}$	0.04 ± 0.01 0.07 ± 0.02		0.07+0.02	0.04 ± 0.01 0.10 ± 0.02			0.18+0.05 0.09+0.08			0.04 ± 0.01 0.07 ± 0.02										
u234* U238 /U238	1.17+0.05	1.30+0.36	1.04+0.10	1.25 ± 0.10		1.00+0.12	1.14+0.06	1.25 ± 0.09		1.17+0.09	1.06+0.13									
_U 238 dpm/g		0.51 ± 0.11	0.40+0.03			0.30+0.03		0.30+0.02			0.56+0.04									
Location	17°54'N, 66°55'W	15°15'N, 68°17'W	12°58'N, 70°4' W	12°9' N, 73°10'W	11°8' N, 76°28'W	9°56'N, 76°20'W	11°50'N, 79°58'W	15°3' N, 81°21'W	17°52'N, 83°41'W	18°39'N, 76°16'W	17°41'N, 73°22'W	16°51'N, 67°34'W	17°53'N, 66°55'W	17°54'N, 66°55'W	15°15'N, 68°14'W	12°46'N, 70°11'W	10°41'N, 65°28'W	11°36'N, 63°36'W	11°40'N, 62°11'W	
Date	21 Nov 71	22 Nov 71	23 Nov 71	24 Nov 71	25 Nov 71	26 Nov 71	29 Nov 71	30 Nov 71	1 Dec 71	2 Dec 71	6 Dec 71	1 Jan 72	l Jan 72	1 Jan 72	2 Jan 72	3 Jan 72	Jan 72	5 Jan 72	Jan 72	
Sta- tion	39 2	41 2	44 2	47 2	48 2.	49 2	51 2	52 3	54	57	29 (65 11	66 21	67 21	68 22	70 23	75† 25	77 26	79† 26	•

^{*} Activity ratio

 $\mathcal{L}_{\mathbf{A}}$ samples were taken with a 6 mesh net except Stations 75 and 79 (20 mesh). \mathbf{A}

Table 2: Concentrations of radionuclides in Caribbean plankton relative to sea water

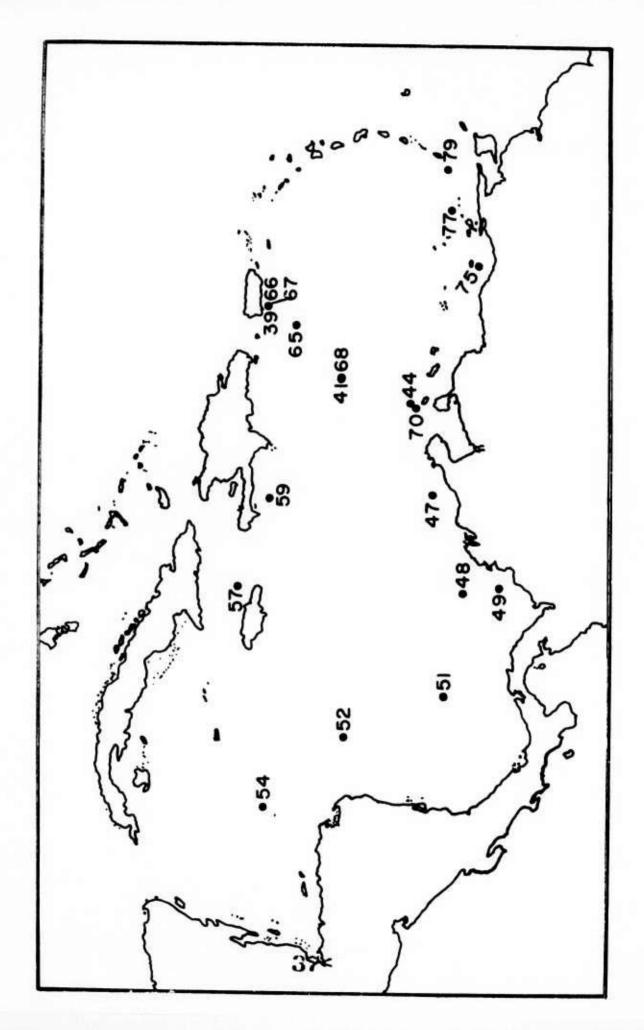
Nuclide	Average activity in dry plankton dpm/g	Surface Caribbean sea water dpm/l	Concentration factor. (liters of sea water equivalent to 1 gram of plankton)
Th ²³²	0.074	< 0.000017	> 4400
Po ²¹⁰	70	0.072	970
Pb ²¹⁰	4.3	0.11	39
Ra ²²⁶	0.29	0.06	4.9
U ²³⁸	0.41	2.4	0.17
Th ²²⁸	0.083	0.0042*	20

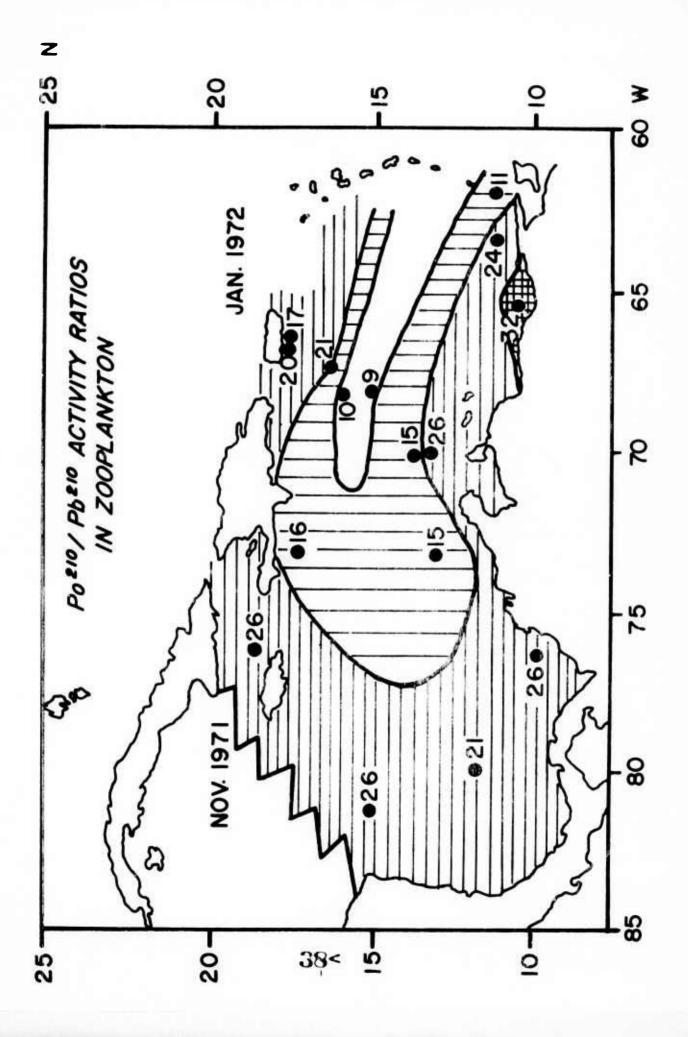
^{*} From Broecker et al. (1973)

Table 3: The estimated $\mathrm{Th}^{228}/\mathrm{Ra}^{228}$ activity ratio of Caribbean plankton

Station No.	Estimated* Ra ²²⁸ dpm/g	Measured Th ²²⁸ dpm/g	Activity ratio Th ²²⁸ /Ra ²²⁸
39	0.14	0.07	0.50
47	0.13	0.10	1.30
51	0.066	0.09	0.73
57	0.061	0.07	0.87

^{*} Estimated Ra 228 is based on Ra 226 and Ra 228 specific activities of 8.5 and 4.0 dpm/100 Kg of sea water (Kaufman et al., 1973), resulting in an activity ratio of Ra 228 /Ra 226 of 0.47. The Ra 226 concentrations in Table 1 are multiplied by 0.47 to arrive at the estimated Ra 228 values.





B. The fates of ${\rm Pb}^{210}$ and ${\rm Po}^{210}$ in the ocean surface.

(In press, <u>Journal de Recherches Atmosphériques</u>)

THE FATES OF ${
m Pb}^{210}$ AND ${
m Po}^{210}$ IN THE OCEAN SURFACE

K.K. Turekian, D.P. Kharkar, J. ThomsonDepartment of Geology and GeophysicsYale University, New Haven, Connecticut 06520

ABSTRACT

The concentration of Pb^{210} and Po^{210} in surface sea water is related to the atmospheric supply rate of Pb^{210} impressed on the supply from the decay of oceanic Ra^{226} on the one hand, and the relative removal fluxes of Pb^{210} and Po^{210} by particle transport to the deep water on the other. The Po^{210}/Pb^{210} activity ratio in marine zooplankton reflects the ratio in sea water which in turn reflects productivity. By using published and new values of Pb^{210} and Po^{210} concentrations in sea water and the partition coefficient of the Po^{210}/Pb^{210} ratio between plankton and surface sea water we are able to calculate the atmospheric flux of Pb^{210} at different oceanic sites. The mean residence times of Pb^{210} and Po^{210} in the mixed layer have also been calculated for these sites. It is proposed that a Po^{210} flux from the ocean surface to the atmosphere may supply at least some of the excess Po^{210} detected over continental areas.

Introduction

There is an excess of Pb^{210} in the surface waters of most of the open ocean over that expected from equilibrium with Ra^{226} by a factor of two to three. The source of this excess Pb^{210} is the atmosphere where Rn^{222} , supplied from the continents, decays to Pb^{210} and becomes part of the aerosol burden. By radioactive decay Pb^{210} (22 year half life) is transformed to Bi^{210} (5 day half life) and then to Po^{210} (138 day half life). The activities of Bi^{210} and Po^{210} in the atmosphere will depend on the mean residence time of aerosols. The Bi^{210}/Pb^{210} activity ratio in the atmosphere is higher than the Po^{210}/Pb^{210} activity ratio because of the approximately 5 day mean residence time of aerosols in the main part of the troposphere [1, 2].

The surface layer of the ocean attains a Pb^{210} activity which is the reflection of atmospheric supply rate, deep ocean supply rate (from Ra^{226} decay) and extraction rate to depth by adsorption on plankton and other particles.

In this paper we use the observed distribution of Pb^{210} and Po^{210} in plankton and sea water to determine the flux of Pb^{210} from the atmosphere to the ocean, the mean residence times of Pb^{210} and Po^{210} in the mixed layer of the oceans, and the Po^{210} flux from the ocean to the atmosphere.

The Pb 210 and Po 210 activities of plankton and ocean surface water

There have been several regional studies of the Pb^{210} and Po^{210} activities of marine plankton. Shannon et al. [3] have reported results off South Africa and Beasley et al. [4] have some results primarily from the Straits of Juan de Fuca in the eastern North Pacific. The levels reported

in both these papers are very similar to each other for zooplankton (Table 1). Only Shannon et al. have analyzed phytoplankton from the same region as the zooplankton and generally they find that although the ${\rm Pb}^{210}$ activities of both phytoplankton and zooplankton are the same, the phytoplankton contains markedly less ${\rm Po}^{210}$ than the zooplankton.

The samples we have analyzed are primarily zooplankton from various locations in the Atlantic Ocean (Table 1) and the Caribbean. We have reported on the Caribbean results elsewhere [5]. The Pb²¹⁰ values of plankton obtained from the center of the Atlantic gyres and the Caribbean are higher than the values from the high productivity regions off the eastern United States which are more comparable to those of Beasley et al. [4] and Shannon et al.

[3] from similarly high productivity regions.

Figure 1 is a representation of the distribution of the Po^{210}/Pb^{210} activity ratio in zooplankton in the Atlantic Ocean based on our data (Table 1 and the Caribbean results from [5]) and those of Shannon et al. [3].

The following features are accentuated in Figure 1: (1) Close to the eastern North American continent the Po²¹⁰/Pb²¹⁰ ratios are low - generally less than 10. (2) The ratio increases abruptly from the coastal region to the oceanic side of the Gulf Stream and is highest at the center of the major gyre systems. (3) The Po²¹⁰/Pb²¹⁰ ratios in the eastern Atlantic are low because of upwelling induced high productivity. (4) The equatorial region is intermediate between the low values of the highly productive margins of the basins and the high values typical of the low productivity regions of the interior of the gyres. (5) The waters north of the Gulf Stream are also low because of high productivity.

In Table 2 the data for the Po^{210} and Pb^{210} concentrations in associated sea water and zooplankton are given for several oceanic areas. The (Po^{210}/Pb^{210}) activity ratio-plankton (Po^{210}/Pb^{210}) activity ratio-seawater ratio ranges between 16 and 25. Clearly, if zooplankton are responsible for the transport of Pb^{210} and Po^{210} from the surface waters to depth, then the efficiency of transport will be greater for Po^{210} . It is this fact combined with the very low Po^{210}/Pb^{210} activity ratios of atmospheric aerosols (about 0.1) that allows the possibility of calculating the fluxes through the mixed layer of the oceans.

The fluxes of Pb^{210} and Po^{210} through the oceanic mixed layer

If we consider a mixed layer in the oceans from 0 to 100 meters depth in which only vertical transport of Pb^{210} and Po^{210} occurs, we can write the steady state budget of Pb^{210} for one square centimeter of the ocean as:

$$R_{Ra} + R_{Pb} = \lambda_{Pb} N_{Pb} + k_{Pb} N_{Pb}$$
 (1)

where R_{Ra} = rate of Pb²¹⁰ supply from Ra²²⁶ decay in a volume 100 meter depth by one square centimeter (i.e. 10 liters)

 R_{Pb} = rate (atoms per minute of Pb^{210} supply from atmospheric aerosols per cm² of ocean surface,

 $\lambda_{\rm Pb}$ = decay constant for Pb²¹⁰,

 $k_{Pb}^{}$ = first order constant for unidirectional particulate transport of Pb^{210} from the mixed layer to depth,

 N_{Pb} = total number of atoms per cm² of Pb²¹⁰ in 100 meter of ocean (i.e. 10 liters).

similarly for Po²¹⁰:

$$\lambda_{Pb}N_{Pb} + R_{Po} = \lambda_{Po}N_{Po} + k_{Po}N_{Po}$$
 (2)

where:

 R_{Po} = rate (atoms per minute) of Po^{210} supply from atmospheric aerosols per cm² of ocean surface,

 $\lambda_{Po} = \text{decay constant for Po}^{210}$,

 k_{Po} = first order constant for unidirectional particulate transport of Po²¹⁰ from mixed layer to depth,

 N_{Po} = total number of atoms per cm² of Po²¹⁰ in 100 meter of ocean (i.e. 10 liters).

To simplify we assume that $\rm R_{PO}$ is very small compared to $\rm \lambda_{Pb}N_{Pb}$ since the activity of $\rm Po^{210}$ relative to $\rm Pb^{210}$ in aerosols is about 0.1 [1] and, as we shall see, the net $\rm R_{PO}$ may be very small compared to the particulate flux in the ocean column.

An estimate of R_{Ra} can be made based on the measured Ra^{226} activity in the surface water. We know from the data of Craig et al. [8] and unpublished data from our laboratory that deep water upwelling to form surface water can be depleted in Pb^{210} relative to Ra^{226} . We have chosen a Ra^{226} activity for 10 liters of water equal to 0.6 dpm, and arbitrarily assumed that 2/3 of this value is the standing crop of Pb^{210} from the supply to the surface of deep water. The Pb^{210}/Ra^{226} activity ratio may actually be less than this because of radon loss to the atmosphere.

With these approximations we can combine the equations for ${\rm Pb}^{210}$ and ${\rm Po}^{210}$ to obtain an expression relating the atmospheric ${\rm Pb}^{210}$ flux to the other parameters:

$$R_{Pb} = A_{Pb} \left[1 + \frac{1}{\alpha} \frac{\lambda_{Po}}{\lambda_{Pb}} \left(\frac{1}{(A_{Po}/A_{Pb})} - 1 \right) - 0.4 \right]$$
 (3)

where: A_{Pb} and A_{Po} are the activities in sea water of Pb^{210} and Po^{210} respectively, in dpm per cm² from the surface to a depth of 100 meters, and $\alpha = k_{Po}/k_{Pb}$.

Thus we can obtain an estimate of the atmospheric aerosol flux of ${\rm Pb}^{210}$ to different parts of the ocean if we know the values ${\rm A}_{\rm Pb}$, ${\rm A}_{\rm Po}$ and ${\rm a}$ for the general area. If we take a large enough area we can ignore any horizontal fluxes as a first approximation. An estimate for ${\rm a}$ can be obtained for a region using the values for zooplankton and sea water as shown in Table 2. Generally in areas of high and average productivity the value of ${\rm a}$ will be assumed to be about 20. The values of ${\rm a}$ based on plankton values in the low productivity centers of the major ocean gyre systems may not be a true index of the ${\rm Po}^{210}/{\rm Pb}^{210}$ activity ratio of the actual downward particulate flux. The flux is small and recycling in the nutrient depleted surface waters may yield an enhanced enrichment of Po in the surface material.

If we confine ourselves to the oceanic marginal areas (but <u>not</u> immediately coastal waters) we can calculate the atmospheric Pb 210 flux and consequently the values of \mathbf{k}_{Pb} and \mathbf{k}_{Po} for a specific region from the available data. The reciprocals of the \mathbf{k}_{Pb} and \mathbf{k}_{Po} can then be taken as the mean residence times τ_{Pb} and τ_{Po} . These are listed in Table 3 for three large areas of the ocean for which sufficient data exist for such a calculation.

The most important observations are: (1) the Pb 210 activity of surface water is not related to the Pb 210 flux from the atmosphere, and (2) the mean residence times of Pb 210 and Po 210 in areas of high productivity are

shorter than in areas of low productivity.

Our results indicate that the deposition rate of ${\rm Pb}^{210}$ from the atmosphere is not expected to be constant at any one latitude. It is a function not only of the radon flux in the area from which the air mass arrives but also of the length of time the air mass takes to arrive at a particular geographic location and perhaps most important of all the efficiency of scavenging of ${\rm Pb}^{210}$ out of the air by aerosols and precipitation at different points along the route. We believe that our type of calculation using the ${\rm Po}^{210}$ and ${\rm Pb}^{210}$ activities provides both the best estimate of the ${\rm Pb}^{210}$ downward flux from the atmosphere to the ocean surface at each location and also the mean residence times of ${\rm Pb}^{210}$ and ${\rm Po}^{210}$ in the upper layer of the ocean. In this our calculations are different from those of Nozaki and Tsunogai [10] who hold the ${\rm Pb}^{210}$ flux constant along a latitude.

The possibility of a significant Po^{210} flux to the atmosphere from the sea

Poet et al. [1] and Moore et al. [2] argue that there is an excess ${\rm Po}^{210}$ burden in the continental atmosphere above that permitted by the ${\rm Bi}^{210}_{-{\rm Pb}}^{210}$ calculation of atmospheric mean residence times of ${\rm Pb}^{210}$ and its daughters. If we assume that ${\rm Bi}^{210}$ and ${\rm Pb}^{210}$ activities in Boulder, Colorado measured by Poet et al. [1] define the first order aerosol downward removal flux constant (λ_R) we arrive at a value of 1.29 x 10^{-4}_{-} min $^{-1}$.

For the troposphere if there is a Po^{210} flux upward from the Earth's surface then for the steady state:

$$N_{Bi}\lambda_{Bi} + R_{Po\uparrow} = N_{Po}\lambda_{Po} + N_{Po}\lambda_{R}$$
 (4)

where: λ_{Bi} and λ_{Po} are the decay constants of Bi²¹⁰ and Pb²¹⁰ respectively,

 ${\rm N_{Bi}}$ and ${\rm N_{Po}}$ are the atoms per unit volume of ${\rm Bi}^{210}$ and ${\rm Pb}^{210}$ respectively,

 $\lambda_{\rm R}$ is the downward removal constant = 1.29 x 10⁻⁴ min⁻¹, and $R_{\rm Po\uparrow}$ is the upward flux of Po²¹⁰ from the earth, equal to 4.57 dpm/100 m³(STP).

If we assume that there is $0.8 \text{ m}^3(\text{STP}) \text{ cm}^2$ of air in the troposphere then an upper value of $R_{\text{Po}\uparrow}$ in terms of the total troposphere per unit area is 0.037 atoms $\text{Po}^{210} \text{ cm}^{-2} \text{ min}^{-1}$. Poet et al. [1] and Moore et al. [2] argue that this upward flux may be ascribable to land derived soil type material wafted upwards with equilibrium activities of Pb^{210} , Bi^{210} and Po^{210} . We suggest that this flux could also be ascribed to Po^{210} derived from the ocean surface and transported to the continents as part of the marine aerosol burden.

We have no analyses of the postulated polonium-bearing particles released from the ocean surface. We can get an estimate of the flux of the presumed polonium carrier - organic material which provides the large surface necessary for efficient polonium adsorption from sea water - by considering plankton. The highest Po²¹⁰ concentrations in plankton are found in the center parts of the warm water gyres of the oceans. A value of 150 dpm/g (dry weight basis) would represent an average of the high values from this region (Table 1). If this were a source of Po²¹⁰ to the atmosphere and hence to the continents, it would imply a rate of mass of plankton-type material released to the atmosphere of 0.3 mg/cm²/year of ocean surface (since the ocean surface is twice the continental surface for which the deficiency was calculated). The actual specific activity of Po²¹⁰ in the aerosol-forming material derived from the ocean

surface is not yet known but if it is higher than our assumed value, then this would diminish the assumed organic flux.

A test of the model of ${\rm Po}^{210}$ supply to the atmosphere should be possible by sampling oceanic air. Such air should have even a higher ${\rm Po}^{210}/{\rm Pb}^{210}$ activity ratio than that found in continental air for the aerosol mean residence time calculated from the ${\rm Bi}^{210}-{\rm Pb}^{210}$ pair. Possible examples of this have been found in Hawaii [11] and in the Antarctic [12],

Acknowledgments

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Table 1: Pb^{210} and Po^{210} in zooplankton from the Atlantic Ocean

S	Sample	Location	Date	Source	Comments	$\frac{\mathrm{Pb}}{\mathrm{dpm/g}}$	Po 210 dpm/g dry wt.	$\frac{210}{\text{Po}}$	
-	7-M	M, ET, 99 N, 77, 07	Mar 28 72	<i>α</i>	1900 GMT	0.38+0.05	4.4+0.8	20 + 1	
2	M-6	41°44'N 64°02'W	Mar 29 72	E	0630 GMT	0.23 ± 0.01	4.5±0.3	21 + 1	
m 	W12C	see comments		:	0745 to 1900 GMT for different tour Combination of 6 tours between 40°6.4'N 41°6.0'W and 42°53'N 58°30'W	0.56±0.09	2.2±0.8	30 + 2	
> -	G0S 2	31°47'N 80°30'W	Feb 4 71	اه.	0-15m 6 mesh oblique tow	1.9 ± 0.2	ſ	1	
5	. 3	31°41'N 80°12'W	Feb 5 71	z	0-30m	1.4 +0.6	95 + 9	68 + 30	
9	9	31°18'N 78°27'W	Feb 6 71	2	0-20m	3.5 ±0.8	196 ± 22	56 ± 14	
7	AII60-25	32°58'S 30°31'W	Apr 13 71	=	300m Midnight tow	3.3 ±0.5	97 ± 10	29 ± 5	
80	-116	05°28'S 08°33'E	June 15 71	:		2.5 ±0.1	17 ± 2	8.0+8.9	
6	-118	02°50'S 08°05'E	June 16 71	÷	11	4.4 +0.6	1	1	
10	-121	00°26'N 17°23'W	June 28 71	E	E E	1.2 ±0.3	34 + 4	28 + 8	
11	-122	00°10'S 34°31'W	July 3 71	Ε		5.0 +0.8	102 ± 9	20 ± 4	
12	AI162-5	28°43'N 62°36'W	Oct 7 71	E	IDOE-17	6.1 +0.4	ı	ı	
13	9-	28°37'N 62°28'W	Oct 7 71	E	IDOE-18	2.6 ±0.1	86 + 4	33 + 2	
14	-7	25°05'N 62°36'W	Oct 971	=	IDOE-20	1.9 ±0.2	91 + 6	9 + 87	
15	-13	35°57'N 64°41'W	Oct 16 71	E	IDOE-42 Sargassum	2.2 ± 0.4	164 + 8	75 ± 14	

Table 1 (cont.):

						$_{\mathrm{Pb}}^{210}$	200	P_{o}^{210}/P_{b}^{210}
						dpm/g	dpm/g	activity
Sample	a 1	Location	Date	Source	Comments	dry wt.	dry wt.	ratio
16 BF 1		33°44'N 75°28'W	Nov 6 72	ပ	1550 EDT 1/2 hour tow	0.4+0.2	33 ± 1	83 + 41
17 "	" 2 34°	34°18.4'N 75°33.5'W	Nov 6 72	=	2030 EDT 1 hour tow	1.3+0.1	30 ± 1	23 ± 2
18 BWP 1		39°45N 74°05'W	July 10 72	اœ	Barnegat Light,N.J.∿2 mi. off shore	0.9±0.4	2.6±0.2	3 + 1
19	2	:	July 10 72	= 1	=	1.0+0.8	3.6+0.3	3 + 3
20	3 3	38°56'N 74°51'W	July 11 72		Cape May, N.J.	0.4+0.1	1.6+0.1	4 + 1
21	4 3	38°19'N 75°04'W	July 12 72	ε	Ocean City,Md. "	0.4+0.1	3.3+0.1	8 + 2
22	5 3	M,07,92 N,88,78	July 14 72	F .	Beaufort, N.C. 4 mi. off shore	2.2+0.7	29 ± 1	13 + 4
23	9	36°50'N 75°57'W	July 16 72	=	Virginia Beach,Va.∿2 mi. off shore	0.8+1.0	7.3±0.4	9 ± 11

Dr. R. Barber, Duke University Marine Station; d: J. Thomson and T. Eisensmith, Yale. a: Dr. A. Walton, Bedford Institute of Oceanography; b: Dr. G. Harvey, Woods Hole Oceanographic Institution; c: Source:

Table 2: The Po 210 and Pb 210 average concentrations in surface sea water, the Po $^{210}/\text{Pb}^{210}$ activity ratios in plankton and sea water and the values of α

		Sea w	*		Plankton .		
Region	dpm/1	dpm/1	Po ²¹⁰ /Pb ²¹⁰	Source	Po ²¹⁰ /Pb ²¹⁰	Source	α
Eastern South Atlantic	0.084	0.044	0.52	[3]	12	[3]	23
Caribbean	0.11	0.072	0.65	<u>a</u>	16	[5]	25
Eastern North Pacific	0.10	0.084	0.84	<u>b</u>	13	[4]	16
Western Pacific	0.092	0.063	0.68	[7]	_		

^{*} Activity ratio

 $\alpha = (Po^{210}/Pb^{210})$ activity ratio-plankton / (Po^{210}/Pb^{210}) activity ratio-sea water

Notes:

- <u>a</u> Values obtained by present authors for a sample from Bermuda collected in March 1973.
- b Po²¹⁰ value from Folsom, T.R., Pillai, K.C. and Beasley, T.M. (1966)
 University of California; IMR-TR-922-66-A, B, C. cited in Beasley et al. [4].
 Pb²¹⁰ value from Rama et al. [6].

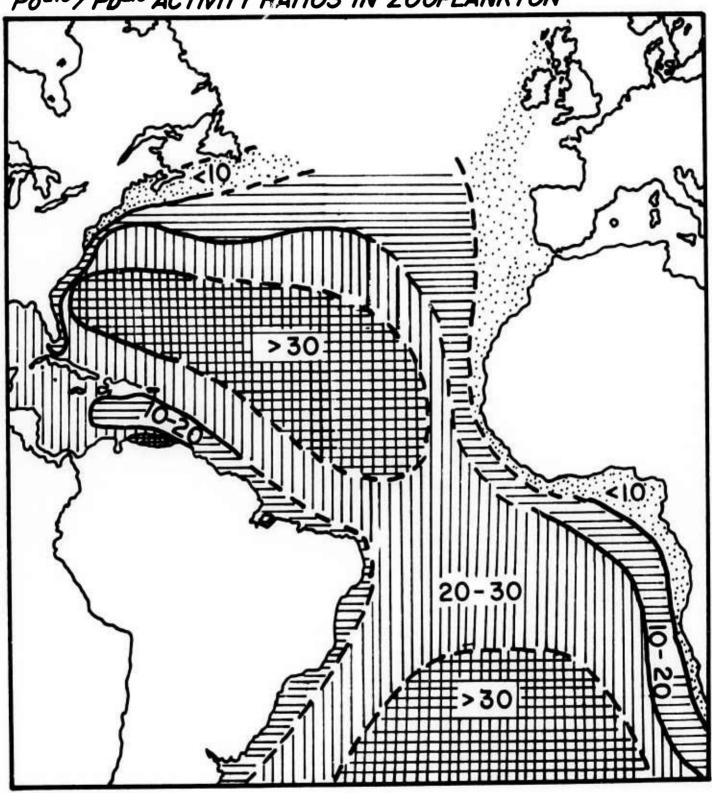
Table 3: Estimates of the atmospheric Pb^{210} flux (R_{Pb}) and the mean residence times of Pb^{210} and Po^{210} in surface waters from various oceanic regions. (α is assumed to be 20).

Region	Source of data	R _{Pb} (dpm cm ⁻² y ⁻¹)	^T Pb (years)	^T Po (years)
West Pacific	[7]	0.053	24	1.2
Eastern South Atlantic	[3]	0.10	9.4	0.41
Caribbean	This paper [5]	0.076	20	1

Figures

Figure 1: The Po²¹⁰/Pb²¹⁰ activity ratio in zooplankton from the Atlantic Ocean. Data and locations in Table 1 and References [3] and [5].

PO 210 / Pb210 ACTIVITY RATIOS IN ZOOPLANKTON



C. ${\rm Pb}^{210}$ in coastal waters of the eastern United States.

(To be submitted to Nature)

Pb 210 IN COASTAL WATERS OF THE EASTERN UNITED STATES

J. Thomson and K. K. Turekian

In this paper we present data on the Pb^{210} activities in coastal waters of the eastern United States between Long Island Sound and Beaufort, North Carolina (Table 1). Coupling these data with the Pb^{210} and Po^{210} activities in plankton collected at the same time as the water, it is possible to estimate the atmospheric Pb^{210} flux to the ocean surface and the mean residence time of Pb^{210} in the mixed layer in the manner described by Turekian et al. (1974). In that work calculations were made for large areas of the ocean such as the eastern Caribbean, the western Pacific and eastern South Atlantic oceans in order to minimize the effects of time variation and horizontal fluxes. Coastal waters can be expected to show greater variability for both the Pb^{210} supply from the atmosphere and the productivity which determines the mean residence time of Pb^{210} in the surface ocean.

The sea water samples were transported to the laboratory where, without filtering, they were acidified to a pH of about 2. The samples sat for several months before processing so no attempt at measuring the initial ${\rm Po}^{210}$ in the water samples was made. Other experiments on coastal waters indicated that the particulates present in the water are mainly detrital and do not seriously influence the ${\rm Po}^{210}$ and ${\rm Pb}^{210}$ activities of the water phase on acidification. The measured ${\rm Po}^{210}/{\rm Pb}^{210}$ activity ratio in plankton associated with the water samples analyzed for ${\rm Pb}^{210}$ can be converted to a ${\rm Po}^{210}/{\rm Pb}^{210}$ activity ratio for the water by assuming that the ${\rm Po}^{210}/{\rm Pb}^{210}$ activity ratio of plankton relative to that ratio in sea water is 20 as determined earlier for large oceanic areas (Turekian et al.,

1974).

With these data we calculate the atmospheric flux of ${\rm Pb}^{210}$ (R $_{\rm Pb}$) to the ocean surface by the equation:

$$R_{pb} = A_{pb} \left[1 + \frac{1}{\alpha} \frac{\lambda_{po}}{\lambda_{pb}} \left(\frac{1}{A_{po}/A_{pb}} - 1 \right) \right] - 0.4$$

where A_{Pb} and A_{Po} are the activities of Pb²¹⁰ and Po²¹⁰ respectively in a volume of 1 cm surface by 100 meters depth (i.e. 10 liters), α is the concentration factor of Po²¹⁰ relative to Pb²¹⁰ and set at 20; and λ_{Pc} and λ_{Pb} are the decay constants for Po²¹⁰ and Pb²¹⁰ respectively. The value of 0.4 represents the ocean water Ra²²⁶-supported Pb²¹⁰.

The values for R_{pb} in dpm/cm²/year are presented in Table 1. The value of R_{pb} refers to an average value for an unspecified period prior to sampling and probably does not refer to an annual average rate. The important feature to note is that the samples south of Delaware Bay are about 5 to 10 times lower than the values to the north. Our interpretation of this observation is that, at least for the unspecified length of time to which the data speak, the air mass over the scathern coast came from a more oceanic source and traversed more moist land (wich low Rn diffusion) than the air mass over the northern coast. This is compatible with the patterns of air movement affecting the east coast of the U.S. The northern area receives air from the relatively arid interior U.S. and has been enriched in radon from which the Pb²¹⁰ is ultimately derived. The farther south along the coast one goes the greater the marine air component, depleted in radon, that passes over the region.

We can also arrive at a value for the extraction constant, $\boldsymbol{k}_{p_h},$ of

 ${\rm Pb}^{210}$ from the surface waters by plankton at each station from the relation-ship:

$$R_{Pb}$$
 (atm) + $R_{Ra} = \lambda_{Pb} N_{Pb} + k_{Pb} N_{Pb}$

Since we have assumed R_{Ra} is 0.4 atoms/cm²/min for a 100 meter depth water column and $R_{\mbox{Pb}}$ (atm) has been determined, the value of $k_{\mbox{Pb}}$ can be obtained for each station. The reciprocal of $\boldsymbol{k}_{\mbox{\scriptsize Pb}}$ is $\tau_{\mbox{\scriptsize Pb}}$, the mean residence time of ${\rm Pb}^{210}$ in the coastal water relative to extraction and removal by plankton. These values are also given in Table 1. The southerly stations show larger mean residence times than the northern stations. The largest mean residence time is for a sample taken most remotely from the coast and has the highest salinity of the samples studied. The $\tau_{\rm ph}$ can be taken as an index of productivity which can vary with time and location. The value of $\tau_{\mbox{\scriptsize Ph}}$ at any one station should be relatable to all the other factors observed to be indices of productivity. The value of $\boldsymbol{\tau}_{p_{\mathbf{0}}}$ is determined by our choice of the value of α = 20. It ranges from 0.06 for the Long Island Sound to 1 for the farthest off-shore sample at Beaufort. These low values are comparable to the mean residence times for Th 228 determined by Broecker et al. (1973) in the western Atlantic closest to shore. This implies that ${
m Th}^{228}$ and Po^{210} have similar modes of particulate transport out of the surficial biologically productive zone but Pb 210 has a longer mean residence time resembling that of the nutrients.

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Corrected* Pb 210 (dpm/1) for assumed Po 210/Pb 210 ratic						
Sea water Measured dpm Po 210/1 13 months after collection	0.043 +0.003	0.080	0.090	0.043 +0.003	0.032 +0.003	0.092 +0.005
Assumed Po ²¹⁰ /Pb ²¹⁰ activity ratio (α=20)	0.095	0.15	0.20	0.40	0.45	0.65
Po 210 Pb 210 activity ratio	1.9+0.9	3 +2	4 +1	8 +2	9 +11	13 ±4
dpm/g(dry wt) Pb 210 Po 210	0.8+0.4 1.5+0.1	$0.9+0.4 2.6+0.2 \\ 1.0+0.8 3.6+0.3$	0.4 <u>+</u> 0.1 1.6 <u>+</u> 0.1	0.4+0.1 3.3+0.1	0.8+1.0 7.3+0.4	2.2±0.7 29 ±1
Salinity	25.4	28.8	31.0	29.1	23.2	32.1
Lat. & Long.						
	Long Island Sound	Barnegat Light, N.Y.	Cape May, N.J.	Ocean City, Md.		Beaufort, N.C.
				63	} <	

^{*} Calculated Pb 210 activity from Po 210 measured 13 months after collection and the assumed Po $^{210}/{\rm Pb}^{210}$ activity ratio at time of collection.

				,		64	<	
			Long Island Sound	Barnegat Light, N.Y.	Cape May, N.J.	Ocean City,	Virginia Beach, Va.	Beaufort, N.C.
Atmospheric	flux of $Po^{210}(R_{\rm pb})$	(dpm/cm ⁻ /y)	0.42	0.45	0.37	990.0	0.038	690.0
Mean resi-	dence time $(\tau_{\rm Pb})$ of 210 in	water(years)	1.1	1.9	2.7	7.1	0.6	20
	Pb ²¹⁰ (plankton) Pb ²¹⁰ (seawater)		16	10	-1	ω	20	20
Mean resi-	dence time $(\tau_{ m Po})$ of $_{ m Po}^{210}$ in	water(years)	90.0	0.1	0.1	0.4	0.5	1.

D. Ra^{226} in plankton from the Atlantic Ocean.

(Preliminary report)

D. P. Kharkar, J. Thomson and K. K. Turekian

The average Ra²²⁶ concentration in marine plankton has been estimated to range over a factor of 100. Phytoplankton seems to be higher in Ra²²⁶ than zooplankton in the same waters as reported by Shannon and Cherry (1971) and there also appears to be a strong water mass effect in the region of study off South Africa. The phytoplankton from the marginal Agulhas current has about 10 times the activity of phytoplankton towards the center of the South Atlantic gyre.

Szabo (1967) reports values from the region of the Bahamas which, in general, are lower than the average zooplankton values of Shannon and Cherry. Our results (Table 1) cover a wider area of the oceans than either of these two above mentioned studies.

It is evident that the range of our data primarily on zooplankton encompasses the values of both Shannon and Cherry and Szabo. Although we must be cautious about generalizations even with this quantity of data, it appears that Shannon and Cherry's observations about the area of South Africa are generally applicable for the whole Atlantic and adjacent seas. In particular:

- (1) Plankton from the low productivity areas of the oceans are generally lower than those from adjacent high productivity areas except in coastal waters where great variability can occur.
- (2) Phytoplankton enriched samples and $\frac{\text{Sargassum}}{\text{Sargassum}}$ are higher in Ra 226 than associated zooplankton.
 - (3) The average of all samples of zooplankton from the normal or low

productivity regions is about 0.3 dpm $\mathrm{Ra}^{226}/\mathrm{g}$ dry weight.

We are analyzing our samples for barium and silicon to establish what relationship these elements have to the concentration of Ra^{226} in plankton.

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Table 1: Ra^{226} in plankton from the Atlantic Ocean.

	Sample No.*	Ra ²²⁶ dpm/g dry wt.
	A. Yale Results	
1.	Continental margin off Savannah, Georgia	
	GOS 2	1.7 + 0.1
	3	3.3 ± 0.1
	6	$\frac{-}{2.2 + 0.1}$
2.	Continental margin off Beaufort, North Carolina	
	BF 1	0.16+ 0.02
	BF 2	0.17+ 0.01
3.	North Atlantic-Sargasso Sea	
	AII62 6	0.101.0.01
	7	0.18+ 0.01
	13 (Sargassum)	0.05 ± 0.01 1.7 ± 0.1
/.		1.7 <u>+</u> 0.1
4.	North Atlantic - 40°W	
	W - 4	0.38+ 0.05
	6	0.23 ± 0.01
	12C	0.56 ± 0.09
5.	Equatorial Atlantic	
	AII60 116	0.19+ 0.01
	118	0.27 ± 0.05
	121	0.05+ 0.01
	122	0.26+ 0.03
6.	South Atlantic - 30°S	
	AII60 25	0.95 <u>+</u> 0.09
	B. Averages of published results	
1.	Szabo (1967) - Bahamas	0.18
2.	Shannon and Cherry (1971)	
	a. South Atlantic - zooplankton	0.66
	b. South Atlantic - phytoplankton	2.2
	c. Agulhas Current - phytoplankton	17.

Table 1 (cont.)

Sample No.*

Ra²²⁶ dpm/g dry wt.

3. Kharkar et al. (1974) - Caribbean

a. 20 mesh

0.20

b. 6 mesh

0.97

^{*} The exact locations are given in Turekian et al. (1974).

E. Po^{210} and Pb^{210} distribution in ocean water profiles from the eastern South Pacific

(Preliminary report)

1. .

Po²¹⁰ AND Pb²¹⁰ DISTRIBUTION IN OCEAN WATER PROFILES FROM THE EASTERN SOUTH PACIFIC: PRELIMINARY RESULTS

J. Thomson and K. K. Turekian

Introduction

In March 1972, we obtained sea water samples from the southeast Pacific NAVOCEANO cruise (the U.S.S. Bartlett, W. S. Moore, Chief scientist) to the high productivity upwelling region west of Peru. Samples from two profiles were received, one inside the upwelling area, and one to the northwest out of the upwelling. This provided an opportunity to study the Po²¹⁰/Pb²¹⁰ activity ratio variation with depth in adjacent ocean areas with greatly different productivities. In addition, since Ra²²⁶ data already exist for the water column in this area (Chung and Craig, 1973) and additional data will be obtained by other groups participating in the NAVOCEANO cruise, the degree of disequilibrium in the Ra²²⁶-Pb²¹⁰-Po²¹⁰ system may be investigated for different oceanic environments. Craig et al. (1973) showed disequilibrium for the Pb²¹⁰/Ra²²⁶ ratio in deep water of the North Pacific.

Analytical procedures

Aboard ship, water was transferred from the 30 liter Niskin bottles used for sampling into 1/2 gallon polyethylene bottles containing 10 ml concentrated HCl. (The 1/2 gallon bottles were new, and had been precleaned with 6 $\overline{\rm N}$ HCl, and 3 rinses of distilled water.) The resultant pH of storage was 1.2.

On arrival at the lab, the bottles were weighed. 1 ml Fe 3+ carrier (10 mg/ml), 2 ml Pb carrier (39.52 mg as PbCrO $_4/2$ ml) and 1 ml Po 208 spike (\sim 0.24 dpm Po 208 /ml) were added. The bottles were shaken and left to equilibrate, normally for several days. The samples were neutralized to pH 6 or 6.5 (Em 5-10 indicator sticks) with NH $_3$ gas, 5 ml Na $_2$ CrO $_4$ solution (10 g/500 ml) was added, and the sample left overnight to settle. Fe(OH) $_3$ and PbCrO₄, carrying Po and Pb, were filtered off using 47 mm diameter, 0.4 μ Nuclepore filters in a Millipore apparatus with a plastic input funnel. Two filters were sometimes necessary to achieve reasonable filter speeds, about 40 minutes per sample. The precipitate was dissolved off the filters with a jet of 1 $\overline{\text{N}}$ HCl to a final volume of 50-70 ml in a 100 ml Teflon beaker. Approximately 100 mg ascorbic acid was added, a 1/2" diameter Ag disc (masked on one side with Teflon tape) added to the solution, and Po isotopes plated out at 85°C for 3 hours, stirred with a Teflon paddle. The disc was removed, washed with water and finally with acetone. The 1/2gallon bottles were weighed empty to give the mass of water analyzed, 12 g being subtracted for the HCl added to each bottle. Each sample was counted for 1 week on a low background α spectrometer.

The solution remaining after plating was heated to dryness with 1 ml concentrated HNO $_3$ with a few drops of HClO $_4$ added. The residue was dissolved in 25 ml 8 $\overline{\rm M}$ HCl and Fe (and U) removed from the solution on a Dowex Ag 1 x 8 anion exchange column (12 cm x 1 cm, 100-200 mesh). The effluent from the column and 2 x 40 ml 8 $\overline{\rm M}$ HCl washes were heated to dryness. This residue was dissolved in 10 ml 6 $\overline{\rm M}$ HCl, and distilled water added to bring the solution to 1.5 $\overline{\rm M}$ HCl (40 ml). Pb was separated from the solution on a similar ion exchange column to that used in Fe separation, washed with

2 x 30 ml 1.5 $\overline{\rm M}$ HCl, and finally eluted with 2 x 40 ml distilled water. PbCrO₄ was precipitated from the eluate at pH 5 by addition of NaOH and excess Na₂CrO₄, filtered off, dried, and weighed into tared plastic vials. This gave the chemical efficiency for Pb, generally 75-90%.

The PbCrO $_4$ was dissolved in 5 ml 6 $\overline{\rm M}$ HCl, 1 ml Po 208 spike added, and the samples stored for a few months to develop Po 210 . At the end of this time, the solutions were adjusted to 1 $\overline{\rm M}$ HCl, and Po plated onto Ag discs as before. Pb 210 activities were then calculated from the Po 210 ingrowth, obtained by a spectrometry as before. The initial Po 210 analyses were then corrected for ingrowth from this amount of Pb 210 between collection and the first plating.

Two liter samples of doubly distilled water were treated analogously to the sea water samples to determine blanks for the procedure.

Results and discussion

The results to date are restricted to ${\rm Po}^{210}$ measurements uncorrected for potentially added ${\rm Po}^{210}$ from ${\rm Pb}^{210}$ decay between the time of collection and analysis. In the deeper waters where the ${\rm Po}^{210}/{\rm Pb}^{210}$ activity ratio may be one no correction will be necessary. The surface values, where the ratio is generally less than one, without the ${\rm Pb}^{210}$ correction represent upper limits for the reported ${\rm Po}^{210}$ values. When sufficient time has elapsed to process the ${\rm Pb}^{210}$ separates, data will be available for the ${\rm Po}^{210}/{\rm Pb}^{210}$ activity ratio at each depth as well as the corrected ${\rm Po}^{210}$ values.

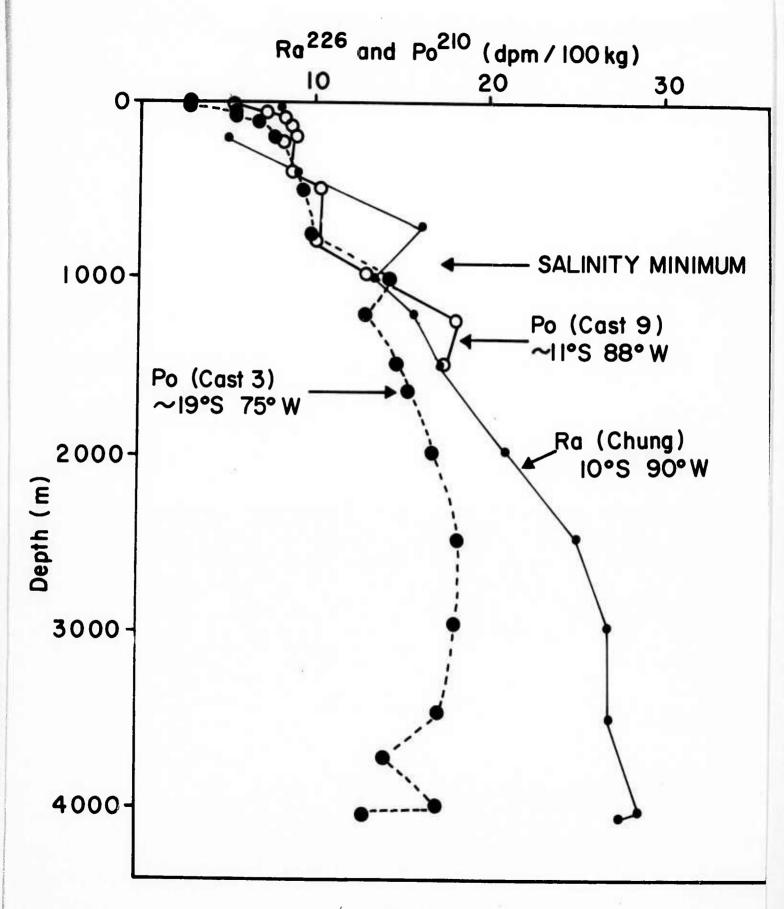
Figure 1 shows a plot of the uncorrected Po^{210} values as a function

of depth at the high productivity station (Cast 3) and the more normal productivity station (Cast 9). The Ra 226 data for that general region are also plotted. It appears that in the region of Cast 9 the Po 210 /Ra 226 activity ratio below about 900 meters is at the equilibrium value whereas a marked deficiency of Po 210 is found under the high productivity zone (Cast 3). This confirms the findings of Craig et al. (1973) with the constraint that we expect the greatest departure from equilibrium for the Pb 210 /Ra 226 system under regions of high productivity where the particle flux through the water column is expected to be the greatest.

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V. APPLICATION TO ARPA INTERESTS

We have shown in the previous section how we can use the relative concentrations of some of the members of the uranium and thorium decay series in the following areas: (1) ocean surface circulation, (2) aerosol derived Pb^{210} flux patterns over the oceans and the possible Po^{210} flux from the ocean to the continents via marine aerosol transport, and (3) the measure of the mean residence times of some of the radionuclides in the surface ocean as a function of surface biological productivity.

In this section we review the relation of these studies to the problem of interest to ARPA that initiated this program: can plankton provide a high energy gamma ray source of high enough flux from natural radioactive nuclides to be detected by towed scintillation crystal γ-ray detectors?

If we consider all the nuclides of Table 1 of Section II, the only potential high energy γ -ray emitter that might be concentrated in plankton is Th²³⁴, which decays to Pa²³⁴ (1.18 minute half life) which then on decay to U²³⁴ emits γ 's as energetic as 1.6 Mev.

As we mentioned earlier it is difficult to obtain ${\rm Th}^{234}$ determination unless the sample is returned immediately to the laboratory after shipboard collection. It is possible, however, to obtain an idea of the maximum ${\rm Th}^{234}$ concentration to be expected from a measurement of the ${\rm Th}^{228}$ concentration in plankton and with a knowledge of the regional ${\rm Th}^{228}$ concentration of surface sea water.

In major parts of the oceans away from coastal regions the ${\rm Th}^{228}/{\rm Ra}^{228}$ activity ratio is about 0.2 (Broecker et al., 1973). In the Atlantic Ocean the average ${\rm Ra}^{228}$ activity in surface water is about 0.02 dpm/1;

hence the ${\rm Th}^{228}$ activity in 0.004 dpm/1. Because of the short half life of ${\rm Th}^{234}$ the ${\rm Th}^{234}/{\rm U}^{238}$ activity ratios of open ocean water is about one (Bhat et al., 1969) and thus the ${\rm Th}^{234}$ activity equals about 2.4 dpm/1. The ${\rm Th}^{234}/{\rm Th}^{228}$ activity ratio in Atlantic surface sea water is then about 600.

If the average excess Th²²⁸ activity of dry plankton is 0.1 dpm/g (Kharkar et al., 1974) and if this thorium were fully scavenged from the ocean by the plankton the Th²³⁴ activity of the dry plankton would be 60 dpm/g. The older the plankton the lower their value would be for the integrated plankton sample because of the decay of already entrapped Th²³⁴ in the aging plankton.

If the total γ activity of the Pa^{234} produced from the Th^{234} is 1% of the β activity which predominates, then a total of 0.6 dpm/g is that maximum γ radiation ascribable to Th^{234}.

Actually in upwelling regions and coastal waters where plankton thrive, the ${\rm Th}^{228}$ and ${\rm Th}^{234}$ activities of the sea water will actually be considerably less than the value we have used, and thus the activities in the plankton would be lower. Since the probability of encountering plankton patches would be greater in these highly productive areas it is clear that such encounters would not yield measurable γ hot spots on towed γ detectors.

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Table 1: The gamma activity contributed by natural radionuclides in plankton (on a dry weight basis).

	Gamma activity (dpm/g)	Gamma energies
Potassium-40 (1)	2.6	1.46 Mev
Protactinium-234		0.765 Mev ∿ 33%
$(from Th^{234}) \qquad (2)$	0.6	1.00 Mev \sim 67%
Polonium-210 (3)	0.001	0.80 Mev

- (1) Assuming 1.3% K in dry zooplankton, $K^{40} = 0.0118\%$ of K and 11% of activity due to gammas emitted on the Ar electron capture branch to Ar^{40} .
- (2) Assuming 60 dpm/g ${\rm Th}^{234}$ (thus ${\rm Pa}^{234}$) activity in dry plankton based on calculation in text and a 1% activity due to gammas.
- (3) Assuming 10^{-5} gammas for one alpha and a Po²¹⁰ α activity of 100 dpm/g dry weight of plankton.